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Molecular modeling of polymers at surfaces

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Abstract

This paper discusses the application of liquid state methods for the molecular modeling of polymeric liquids at solid surfaces. The techniques of integral equation theory, density functional theory, and computer simulation are described and used to investigate the density profiles of polymer melts at smooth surfaces. It is shown that an excellent description of the surface behaviour of polymers can be obtained with only modest computational effort. In particular, the density functional theory is in quantitative agreement with simulation results for a wide range of conditions. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The behaviour of polymers near surfaces is of crucial importance in many practical applications [1]. The obvious examples are in lubrication, adhesion, and coatings where the final product contains polymers at a surface. Polymer surface behaviour is also important in material fabrication. For example, the finish of an extrudate can depend strongly on the interactions between the polymer molecules and the extruder die. Perhaps less obvious is the importance of polymers in the stability of colloidal dispersions [2]. The addition of polymers to colloidal suspensions can either enhance or decrease the tendency of the particles to flocculate depending on the polymer induced forces between the particles. These forces can be qualitatively different depending on the degree of polymer adsorption, the ionization of the polymer (in the case of polyelectrolytes), and molecular architecture (e.g. branching). For these reasons and more, the behaviour of polymers at surfaces has been an area of active research for many decades.

It is widely accepted that in most of the applications mentioned above the behaviour of the polymer molecules within a few nanometers (or even Angstroms) of the surface plays an important role. Advances in experimental techniques have allowed one to probe these systems on molecular lengthscales [3] and this has spurred theoretical research in this area. In this paper I describe techniques for the molecular modeling of polymers at surfaces. I focus on equilibrium static properties and discuss the implementation computer simulation and theoretical methods to describe the density profiles of polymers at surfaces.

The simplest problem concerning the surface behaviour of polymers is the structure of the liquid at a smooth solid surface. Computer simulations of polymers at surfaces have been popular [4–8] but, because they are computationally intensive, have been restricted to rather simple models of polymers. Liquid state theories for this problem include density functional theories [9–15] and integral equations [16,17]. In the integral equation theory the properties of a polymer fluid at a surface are obtained from those of a mixture of polymers and spheres, in the limit as the spheres become infinitely dilute and infinitely large [16]. For dense hard-chain polymer melts this theory is convenient and very accurate, but has some severe deficiencies in some other cases [14]. In the density functional theory [13–15] an approximate expression is used for the free energy of the fluid as a functional of the density profile at a surface. This functional is then minimized to obtain the density profile. The density functional theory is much more accurate than the integral equation theory but suffers from two disadvantages: it is computationally more intensive, requiring several single molecule simulations for each state point of interest, and it is more difficult to obtain quantities such as the solvation force between surfaces. With modest computational effort, however, accurate results for the surface properties of polymers can be obtained. In this paper, I describe integral equation and density functional theories, and compare these to computer simulations for hard chains at hard walls. The rest of this paper is organized as follows: Section 2 describes integral equation theories, Section 3

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describes density functional theories, and Section 4 compares results for the density profiles obtained from the theories to computer simulations.

2. Integral equation theory

2.1. Uniform fluids

A quantity of central importance in the study of uniform liquids is the pair correlation function, $g(r)$, which is the probability (relative to an ideal gas) of finding a particle at position r given that there is a particle at the origin. All other structural and thermodynamic properties can be obtained from a knowledge of $g(r)$. The calculation of $g(r)$ for various fluids is one of the long-standing problems in liquid state theory and several accurate approaches exist. These theories can also be used to obtain the density profile of a fluid at a surface.

The starting point is the Ornstein–Zernike (OZ) equation which, for a one-component system of liquids interacting via spherically symmetric potentials (e.g. Argon), is [18]

$$h(r) = c(r) + \rho \int \mathrm{d}\mathbf{r}' c(\mathbf{r}') h(|\mathbf{r}-\mathbf{r}'|), \tag{1}$$

where ρ is the number density of the fluid, $h(r) \equiv g(r) - 1$ is the total correlation function, and $c(r)$ is the direct correlation function, defined via Eq. (1). In Fourier space the OZ equation may be written as:

$$\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k) \hat{h}(k), \tag{2}$$

where the three dimensional Fourier transform is defined via

$$\hat{h}(k) = \frac{4\pi}{k} \int_0^\infty r \sin(kr) h(r) \mathrm{d}r. \tag{3}$$

Eq. (1) cannot be solved by itself because it contains two unknown functions $h(r)$ and $c(r)$. To solve for $g(r)$ one therefore requires another equation, commonly referred to as a "closure" relation. A popular closure approximation is the Percus–Yevick (PY) approximation [18]:

$$c(r) = (1 - \mathrm{e}^{\beta u(r)}) g(r), \tag{4}$$

where $\beta = 1/k_\mathrm{B}T$, k_B is Boltzmann's constant, T is the temperature, and $u(r)$ is the interaction potential. For hard sphere liquids the PY closure is particularly simple:

$$g(r) = 0, \ r < \sigma, \tag{5}$$

$$c(r) = 0, \ r > \sigma, \tag{6}$$

where σ is the hard sphere diameter. The PY closure is quantitatively very accurate for the pair correlation function and equation of state of hard sphere liquids (when compared to simulations).

If each polymer is modeled as being composed of N beads (or sites) and the interaction potential between polymers can be written as the sum of site-site interactions, then simple generalizations of the OZ equation to polymers are possible. One approach is the polymer reference interaction site model (PRISM) theory [19] (based on the RISM theory [20]) which results in one non-linear integral equation given by

$$\hat{h}(k) = \hat{\omega}(k)\hat{c}(k)\hat{\omega}(k) + \rho\hat{\omega}(k)\hat{c}(k)\hat{h}(k), \tag{7}$$

$$\hat{h}(k) = \hat{\omega}(k)\hat{c}(k)\hat{S}(k), \tag{8}$$

where ρ is the number density of polymer beads (not chains), $\hat{\omega}(k)$ is the single chain structure factor, $h(r)$ and $c(r)$ are the total and direct correlation functions, respectively, averaged over all the beads on the polymers, and $\hat{S}(k) \equiv \hat{\omega}(k) + \rho\hat{h}(k)$ is the static structure factor. The single chain structure factor may be obtained from the intramolecular correlations via

$$\omega(r) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \omega_{ij}(r) \tag{9}$$

where $\omega_{ij}(\mathrm{r})$ is the probability that beads i and j on the same chain are a distance r apart, and N is the number of beads (or sites) on the chains. In the simplest implementation of the PRISM theory, $\hat{\omega}(k)$ is assumed to be known and the standard closure approximations used for simple liquids, e.g. PY, and employed without change.

In the PRISM approach, information regarding chain conformations and local chemistry (e.g. bond angle and bond length constraints, stiffness, and branching) is input through the single chain structure factor, $\hat{\omega}(k)$. In general this function depends on the pair correlations and must be calculated self-consistently with $g(r)$. In most implementations of the theory, however, $\hat{\omega}(k)$ is assumed to be known a priori. This can be justified by invoking the Flory ideality hypothesis, which states that chains in a melt behave essentially like ideal chains because intramolecular interactions exactly counteract intermolecular interactions.

The OZ (or PRISM) equation with closure relation can be solved using a Picard iteration procedure. One starts with a guess for the function $\gamma(r) = h(r) - c(r)$, either $\gamma(r) = 0$ or the value of $\gamma(r)$ from some condition close to the condition of interest. Using the closure relation, $c(r)$ is then obtained from $\gamma(r)$. With the PY closure, for example,

$$c(r) = (\mathrm{e}^{-\beta u(r)} - 1)(1 + \gamma(r)). \tag{10}$$

$\hat{c}(k)$ is then evaluated numerically and the next guess for $\gamma(r)$ is obtained from the OZ equation followed by an inverse Fourier transform of $\hat{\gamma}(k)$. For numerical convenience the functions are discretized and the Fourier transforms are performed using the fast Fourier transform (FFT) algorithm. It is necessary to work with the function $\gamma(r)$ because it is not convenient to perform a numerical Fourier inversion of either $h(r)$ or $c(r)$ because $\hat{h}(k)$ and $\hat{c}(k)$ are long-ranged (in hard sphere liquids, for example, $h(r)$ and $c(r)$ contain step functions).

2.2. *Polymeric fluids at a surface*

Integral equations can also be used to treat non-uniform fluids, such as fluids at surfaces. One starts with a binary mixture of spheres and polymers and takes the limit as the spheres become infinitely dilute and infinitely large [16–22]. The sphere polymer pair correlation function is then simply related to the density profile of the fluid. For a binary mixture of infinitely dilute spheres and polymers the relevant PRISM equation is [16]

$$\hat{h}_w(k) = \hat{S}(k)\hat{c}_w(k), \tag{11}$$

where $h_w(r)$ and $c_w(r)$ are the total and direct correlation functions between the polymer and sphere, and $\hat{S}(k)$ is the static structure factor of the uniform polymer fluid discussed in Section 2.1.

To obtain the PRISM equation for a fluid at a surface Eq. (11) is first transformed to real space using bipolar coordinates, and then the spheres are made infinitely large. In this limit, the correlation functions h_w and c_w become functions only of the perpendicular distance, z, from the surface. The resulting equation can then be transformed to reciprocal space using a one dimensional Fourier transform given by,

$$\tilde{h}_w(K) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} h_w(z)\ \exp(\mathrm{i}z)\mathrm{d}z. \tag{12}$$

The resulting equation, called the wall-PRISM equation, is very simple:

$$\hat{h}_w(k) = \hat{S}(k)\tilde{c}_w(k), \tag{13}$$

which looks just like Eq. (11) except that one-dimensional rather than three dimensional Fourier transforms are used for c_w and h_w. The PY closure is

$$c_w(z) = (1 - \mathrm{e}^{-\beta\phi(z)})g_w(z), \tag{14}$$

where $\phi(z)$ is the fluid-surface potential (or external field), and $g_w(z)=1+h_w(z)$. For a fluid between two hard surfaces (impenetrable to centres of chains sites) located at $z=0$ and $z=H$, the PY closure simplifies to

$$g_w(z) = 0, \quad z < 0 \text{ or } z > H, \tag{15}$$

$$c_w(z) = 0,\ 0 < z < H, \tag{16}$$

The density profile is given by $\rho(z)=\rho g_w(z)$. The wall-PRISM equation is solved by first calculation $\hat{S}(k)$ (e.g. using the PRISM theory) and then employing a Picard iteration procedure for the wall-PRISM equation, similar to the one described earlier for the PRISM equation.

3. Density functional theory

In density functional theory one starts with an approximation for the grand free energy, Ω, as a functional of the density profile. If $\mathbf{R}$ denotes the positions of all the N monomers on a polymer molecule and $\rho_\mathrm{M}(\mathbf{R})$ is the molecular density as a function of these positions, then at equilibrium

$$\frac{\delta\Omega}{\delta\rho_\mathrm{M}(\mathbf{R})} = 0, \tag{17}$$

and this condition determines the density profile.

The functional Ω is related to the Helmholtz free energy functional, $F[\rho_\mathrm{M}]$ via a Legendre transform:

$$\Omega[\rho_\mathrm{M}(\mathbf{R})] = F[\rho_\mathrm{M}(\mathbf{R})] + \int[\Phi(\mathbf{R}) - \mu]\rho_\mathrm{M}(\mathbf{R})\mathrm{d}\mathbf{R}, \tag{18}$$

where μ is the chemical potential and $\Phi(\mathbf{R})$ is the external field. $F[\rho_\mathrm{M}]$ can be expressed as the sum of an (exactly known) ideal part and excess (F^ex) part, i.e.

$$\begin{aligned} F[\rho_\mathrm{M}(\mathbf{R})] = k_\mathrm{B}T\int \mathrm{d}\mathbf{R}\rho_\mathrm{M}(\mathbf{R})[\ \ln\ \rho_\mathrm{M}(\mathbf{R}) - 1] \\ + \int \mathrm{d}\mathbf{R}V(\mathbf{R})\rho_\mathrm{M}(\mathbf{R}) + F^\mathrm{ex}[\rho_\mathrm{M}(\mathbf{R})], \end{aligned} \tag{19}$$

where $V(\mathbf{R})$ describes all the intramolecular interactions. The main approximation in any density functional theory is the expression for the excess free energy functional.

In simple liquids the density profile is a function of only one position variable, and the free energy functional is much simpler [18]

$$F[\rho(\mathbf{r})] = k_\mathrm{B}T\int \mathrm{d}\mathbf{r}\rho(\mathbf{r})[\ \ln\rho(\mathbf{r}) - 1 + F^\mathrm{ex}[\rho(\mathbf{r})], \tag{20}$$

where $\rho(\mathbf{r})$ is the density profile. It is the presence of the $V(\mathbf{R})$ term in the functional for polymers that makes things complicated.

A simple and successful approximation for the excess free energy functional is to first assume the functional is only a functional of the average site density profile, denoted $\rho(\mathbf{r})$, and then invoke the weighted density approximation (WDA) [23,24], i.e.,

$$F^\mathrm{ex}[\rho_\mathrm{M}(\mathbf{R})] \approx F^\mathrm{ex}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})f(\bar{\rho})\mathrm{d}\mathbf{r}, \tag{21}$$

where $f(\bar{\rho})$ is the excess (over ideal gas) free energy per site of the bulk fluid evaluated at a site density $\bar{\rho}(\mathbf{r})$,

$$\bar{\rho}(\mathbf{r}) = \int \rho(\mathbf{r}')w(|\mathbf{r} - \mathbf{r}'|)\mathrm{d}\mathbf{r}' \tag{22}$$

is the weighted density, and $w(r)$ is the weighting function, normalized so that $\int w(\mathbf{r})\mathrm{d}\mathbf{r} = 1$. The function $f(\rho)$ can be obtained from an equation of state. The central approximation is the choice of the weighting function. The most accurate theory [15] employs the Curtin–Ashcroft recipe [25] where $w(r)$ is obtained from

$$\begin{aligned} -k_\mathrm{B}T\hat{c}(k) = 2f'(\rho)\hat{w}(k) + \rho f''(\rho)\hat{w}^2(k) \\ + 2\rho f'(\rho)\hat{w}(k)\frac{\partial\hat{w}(k)}{\partial\rho}, \end{aligned} \tag{23}$$

where primes denote derivatives with respect to density, and the direct correlation function can be obtained from the PRISM theory described in the previous section. Eq. (23) is derived by forcing the free energy functional to satisfy an exact relation between the second derivative of the excess free energy functional and the direct correlation function.

The density functional theory has the structure of a self-consistent field theory where the density profile is obtained from a simulation of a single chain in the field due to the rest of the fluid and the surface. A formal minimization of Ω gives

$$\frac{\delta\Omega}{\delta\rho_{\mathrm{M}}(\mathbf{R})} = \frac{\delta F}{\delta\rho_{\mathrm{M}}(\mathbf{R})} + \Phi(\mathbf{R}) - \mu = 0, \tag{24}$$

which may be written as

$$\rho_{\mathrm{M}}(\mathbf{R}) = \exp\left[-\beta V(\mathbf{R}) + \beta\mu - \beta\Phi(\mathbf{r}) + \beta\sum_{i=1}^{N}\lambda(\mathbf{r}_i)\right], \tag{25}$$

where $\lambda(\mathbf{r})$ is the self-consistent field given by

$$\lambda(\mathbf{r}) = \frac{\delta F^{\mathrm{ex}}}{\delta\rho(\mathbf{r})} = f(\bar{\rho}(\mathbf{r})) + \int \mathrm{d}\mathbf{r}'\rho(\mathbf{r}')\mathrm{w}(|\mathbf{r}-\mathbf{r}'|)\mathrm{f}'(\rho(\mathbf{r}')). \tag{26}$$

If there were no intramolecular interactions (such as bonding or excluded volume) then $V(\mathbf{R})=0$, and the next guess for the density profile can be obtained directly from Eq. (25). The presence of $V(\mathbf{R})$ necessitates either a multi-dimensional integration or (more conveniently) a single chain simulation.

The implementation of the density functional theory entails the iterative solution of one equation

$$\rho(\mathbf{r}) = \int \mathrm{d}R\left[\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\right] \times \exp\left[-\beta V(\mathbf{R}) + \beta\mu - \beta\Phi(\mathbf{R}) + \beta\sum_{i=1}^{N}\lambda(\mathbf{r}_i)\right], \tag{27}$$

with $\lambda(\mathbf{r})$ given by Eq. (26). This equation is solved by discretizing the density profile, treating the value of the density at each point as an independent variable, and then employing a Newton–Raphson procedure (described previously [13]) to solve for the density profile. This sounds more complicated than it really is, and the procedure generally converges within 5–10 iterations.

The density functional theory requires, as input, an equation of state and direct correlation function of the bulk fluid. Accurate equations of state are available for freely-jointed hard chains [26] and fused-hard-sphere chains [15]. The direct correlation function is obtained as follows. The single chain structure factor is first calculated, using the Koyama distribution (as extended to continuous-space chains by Honnell et al. [27]) for the freely-jointed tangent-sphere chains and using single chain simulations of self-avoiding walks for the fused-hard-sphere chains. The direct correlation function is then obtained from the PRISM theory with the PY closure.

4. Monte carlo simulations and test of theories

4.1. Monte carlo simulations

Computer simulations of confined polymers are generally performed in the canonical ensemble where the number of molecules, volume, and temperature are fixed. The reason for this is that simulations in the grand canonical (constant chemical potential) ensemble require the successful insertion of polymer molecules into the fluid, and this is inefficient. In addition, Monte Carlo simulations are generally preferred over molecular dynamics because the intrinsically slow dynamics of polymer melts makes the latter computationally more intensive.

Most simulations to date have been performed for polymers confined between two parallel smooth surfaces. In this paper I discuss the case where the surfaces are far enough apart that a bulk like region is present in the middle region between the surfaces. The simulation cell itself is a rectangular parallelepiped bounded at $z=0$ and $z=H$ by hard walls that are impenetrable to the centres of the sites of the polymer molecules. Two models of polymers are considered: Freely-jointed tangent sphere chains and freely-rotating chains with fixed bond angles ($\theta=109.47°$) and bond lengths ($l=0.4\sigma$). The former is the standard model for polymers and the latter is a simple model for linear alkanes where attractive torsional, and bending interactions are ignored.

The simulation itself proceeds in three phases: initial configuration generation, equilibration, and averaging. Initial configurations are created using a growth and equilibration algorithm [6]. If N_{M} chains are desired, N_{M} monomers are first inserted into the simulation cell. This is generally easily done since the chain density is much lower than the monomer density. The growing process then proceeds through several cycles. In each cycle an attempt is first made to move an existing chain (using methods described below) and then an attempt is made to add a bead to an existing chain provided it is not fully grown. The process is continued until all the chains are grown. The equilibration and averaging phases consist of moving a randomly chosen and accepting or rejecting the move according to the Metropolis criterion. For hard chains this means the move is accepted if there is no overlap with the other chains and rejected otherwise. After a certain number of attempted moves (usually between 100 and 1000) the desired properties (such as the density profile) are calculated and added to a running average. The only difference between the equilibration and averaging phase is that the average properties obtained in the former are not used in calculating the final results. The system is considered to be equilibrated if the density profile is symmetric about the mid-point between the two surfaces.

The important issue in polymer simulations is the selection of Monte Carlo moves. For the hard chain models discussed here, a combination of the three following moves is very successful in evolving the system. The first is reptation [28], where a bead is detached from one (randomly chosen) end of the chain at re-attached at the other end. The second is continuum configurational bias (CCB) [29] where the chain is cut at a particular point and then re-grown in a biased fashion to try and find empty spaces in the liquid. The bias is then removed by appropriately modifying the acceptance criterion. The third is the move of Dickman and Hall (DH) [4,6], where one of the end beads (chosen randomly) is translated, and the rest of the beads are "jiggled" by a small amount while making sure bond length or other constraints are always satisfied. Generally the three moves are chosen with equal probability except at high densities, where the DH move fails and is not used any longer. The CCB and DH moves contain parameters, such as the maximum displacement of a bead, which can be changed to adjust the percentage of accepted moves. This is done so as to maximize the mean square displacement of the chain. Typically about 10% of attempted CCB and DH moves are accepted.

4.2. Density profiles of hard chains

The density profiles of hard chain polymers at surfaces are governed by a competition between packing and con-

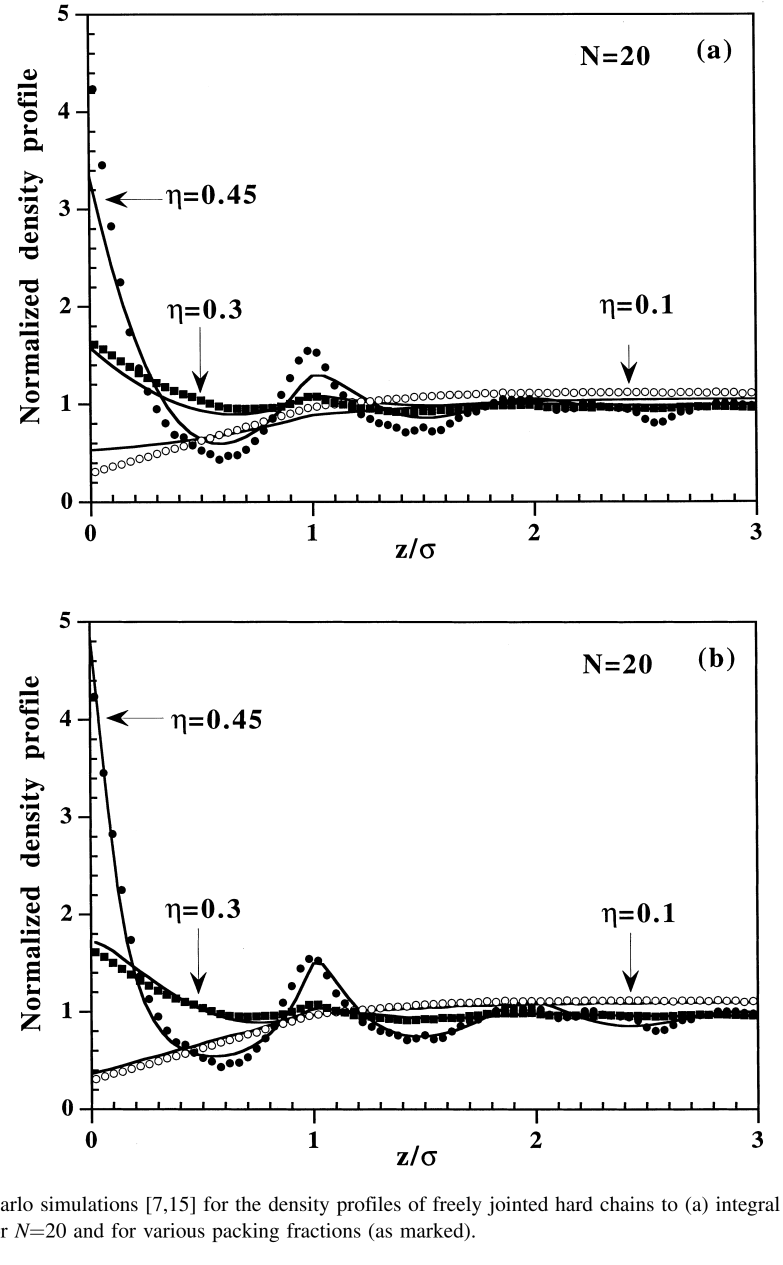

Fig. 1. Comparison of Monte Carlo simulations [7,15] for the density profiles of freely jointed hard chains to (a) integral equation theory and (b) density functional theory predictions, for N=20 and for various packing fractions (as marked).

formational entropic effects [4]. A single chain suffers a loss of configurational entropy near the surface, and this promotes a depletion of chain sites near the walls. On the other hand packing the chains against the surface is a more efficient way to utilize free volume, and this promotes and enhancement of chains sites near the walls. At low densities conformational entropic effects dominate, and at high densities packing entropic effects dominate.

These trends are seen in Fig. 1(a) and (b) which compare predictions of the integral equation and density functional theories, respectively, to simulations of freely-jointed tangent sphere hard chains [7] with N=20, H=10σ, and for various packing fractions, $\eta(\equiv\pi\rho\sigma^3/6)$. The density profiles are normalized to the average value in the cell. Both theories are in qualitative agreement with the simulations and predict depletion and enhancement effects and the transition from one behaviour to the other with increasing density. The integral equation theory tends to overestimate the value of the density at the surface for low densities and underestimate the value of the density at the surface for high densities. The density functional theory, on the other hand, is in excellent quantitative agreement with the simulations at all distances. Note that even for very dense systems the density profiles are relatively flat within a few sphere diameters from the surface.

Similar results are seen for other models of polymers. Fig. 2(a) and (b) compare the integral equation and density functional theories, respectively, to computer simulations for fused-hard-sphere chains at hard walls for N=16, H=10, and for various reduced densities. (For fused hard sphere chains the volume per sphere is roughly $0.28\sigma^3$ and the packing fraction is therefore $\eta\approx0.28\rho\sigma^3$.) The qualitative

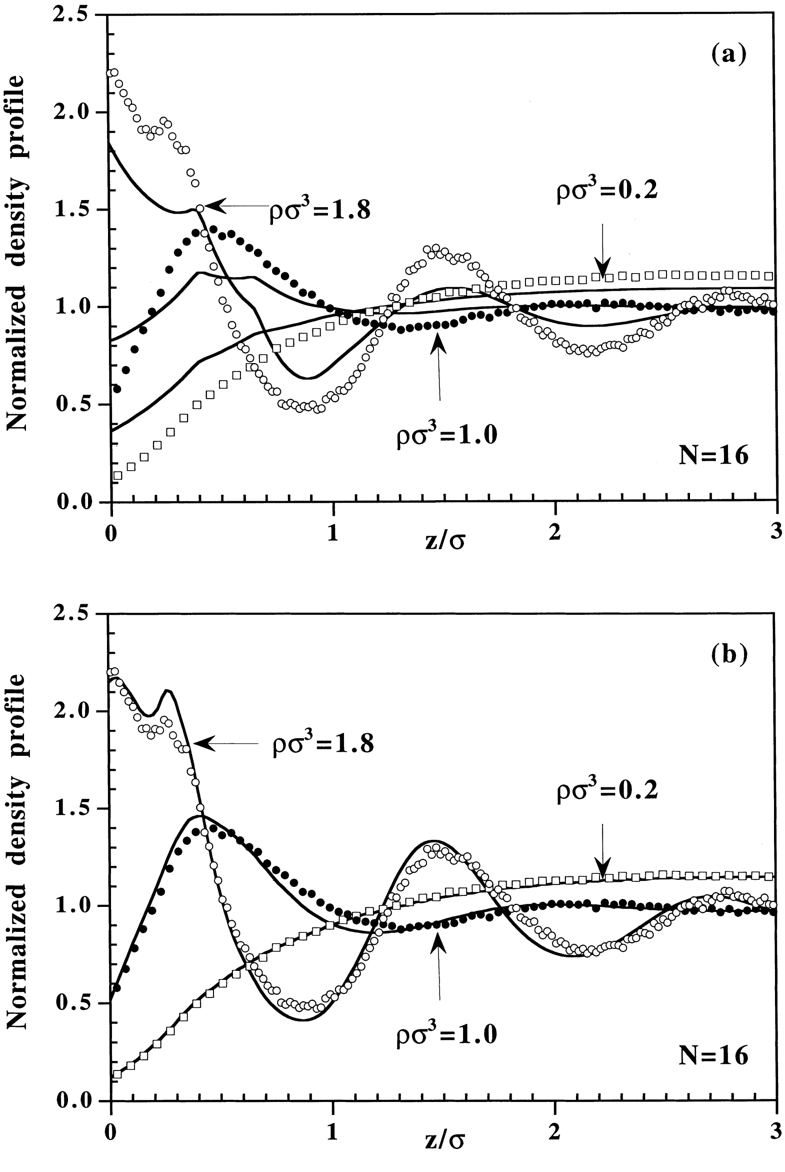

Fig. 2. Comparison of Monte Carlo simulations [15] for the density profiles of fused-hard-sphere freely rotating chains to (a) integral equation theory and (b) density functional theory predictions, for N=16 and for various reduced densities (as marked).

trends are similar to what was seen for the freely-jointed hard chains in Fig. 1. The integral equation theory is in qualitative agreement with the simulations but is quantitatively not very accurate. The density functional theory, on the other hand, is in excellent quantitative agreement with the simulations for all densities and at all distances.

Although the density functional theory is in much better agreement with the simulations it has some disadvantages that must be considered. For one, the theory requires as input an equation of state for the bulk fluid, and for another it requires several single chain simulations for each state point. The integral equation theory does not suffer from these drawbacks: it is simple to use and may be considered an *ab initio* technique. One can conclude therefore that the integral equation theory is well suited to obtaining a quick but rough estimate of the density profiles, but for an accurate description one has to go to the more complicated density functional theory.

5. Summary

The surface behaviour of polymers is of considerable practical and scientific importance. In this paper I have shown that the techniques of computer simulation and liquid state theory can be effectively used to tackle polymeric problems. The implementation of these approaches is more computationally demanding than in simple liquids but the availability of fast computers makes this less of a problem.

For example, I have described a density functional theory for polymers that is extremely accurate for the density profiles of polymers at surfaces, about as accurate as similar theories are for hard spheres at surfaces. The quantitative accuracy of density functional theory is significant because several other features, such as the effect of polymer architecture on the surface forces, are more conveniently investigated using this method. This is important because computer simulations because simulations of these complex models are almost prohibitively expensive. Extensions of these methods to study polar and charged chains are also possible and are under investigation.

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